OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
01 October 1993 through 30 September 1994

R&T Number: 4326806

Contract/Grant Title: N00014-91-J-4057; Computational Studies in Support of Energetic Materials Synthesis

Program Officer: Richard S. Miller

Principal Investigator: Peter Politzer

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New Orleans, Louisiana 70148

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a.	Number of Papers Submitted to Referred Journal but not yet published: (1) Accepted for publication and in press: 1 (2) Submitted for publication, no word yet: 2	3
b.	Number of Papers Published in Referred Journals: (List Attached):	8
c.	Number of Books or Chapters Submitted but not yet Published:	2
d.	Number of Books or Chapters Published (List Attached):	0
e.	Number of Printed Technical Reports & Non-Referred Papers (List Attached):	6
f.	Number of Patents Filed:	0
g.	Number of Patents Granted (List Attached):	0
h.	Number of Invited Presentations at Workshops or Professional Society Meeting (List Attached):	3
i.	Number of Presentations at Workshops or Professional Society Meetings (List Attached):	0
j.	Honors/Awards/Prizes for Contract/Grant Employees: (List Attached, may include Society Awards/Offices, Promotions, Faculty Awards/Offices, etc.)	2

k. Providing the following information will assist with statistical purposes.

PI/CO-PI:	TOTAL	1	Grad Students:**	TOTAL	0
	Female	0		Female	
	Minority*	0		Minority*	
			Post Doc:**	TOTAL	6
				Female	4
				Minority*	2

1. Degrees Granted (List Attached): 0

* Underrepresented or minority groups include Blacks, Hispanics, and Native Americans.
Asians are not considered an underrepresented or minority group in science and engineering.

** Supported at least 25% this year on contract/grant.

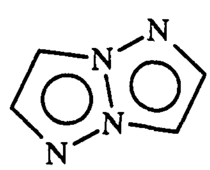
Enclosure (1)

DESCRIPTION OF RESEARCH OBJECTIVES AND RESULTS DURING PAST YEAR

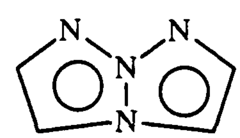
1. Heats of Formation

Earlier, we have developed a procedure for computing standard gas phase heats of formation (see End-of-Fiscal-Year Report, September 1993). It involved Hartree-Fock geometry optimization plus a single-point density functional calculation of ΔE for the formation of the molecule from its elements. This was combined with translational, rotational and vibrational contributions corresponding to 25° C and converted to ΔH, followed by the addition of empirical atomic correction terms. The reason for the Hartree-Fock rather than density functional geometry optimization was that the program used for the latter does not have an efficient optimization routine. While this approach to computing heats of formation is effective and reliable, it would clearly be desirable to obtain the geometry by a density functional technique; this would be more accurate and also would eliminate the extra single-point computation. Recently, a density functional code with an efficient optimization subroutine has become available: Gaussian 92/DFT. We have accordingly revised our procedure to be entirely in terms of this code; this required repeating the computations for all of the compounds in our data base (54), in order to obtain new atomic correction terms. This work has now been completed and the new procedure is operational; it is essentially as accurate as before, but more efficient. The heats of formation of the compounds in the data base are reproduced with both the average absolute error and the standard deviation being less than 4 kcal/mole. This procedure is now being used for computing heats of formation for compounds of interest to ONR, such as the following:

(a) Tetraazapentalenes:



1



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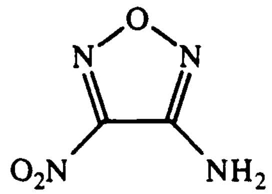
These isomers are the backbones of several energetic compounds that have been or are being synthesized by J. H. Boyer and M. L. Trudell at the University of New Orleans, as well as the compound TACOT, synthesized in 1959 at DuPont. The known derivatives of **1** have an unusual degree of stability, unanticipated in a molecule containing four linked nitrogens. As an initial step in trying to understand the origin of this stability, we have computed the gas phase heats of formation of **1** and **2**. Both are very high, around 125 kcal/mole. Accordingly we are proceeding to investigate other possible reasons for the stabilities of the derivatives of **1**.

(b) Aminonitrofurazan:



3

This compound has been prepared by J. H. Boyer. We find its gas phase heat of formation to be 43 kcal/mole, or 330 cal/g. For comparison, the corresponding value for RDX is 206 cal/g.

2. Difluoramines

We have finished a comparative computational analysis of a group of difluoramines and the corresponding nitramines, **4** - **9**.

$(H_3C)_2N{-}NF_2$

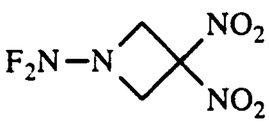
4

$(H_3C)_2N{-}NO_2$

5

6

7



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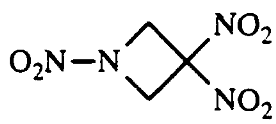
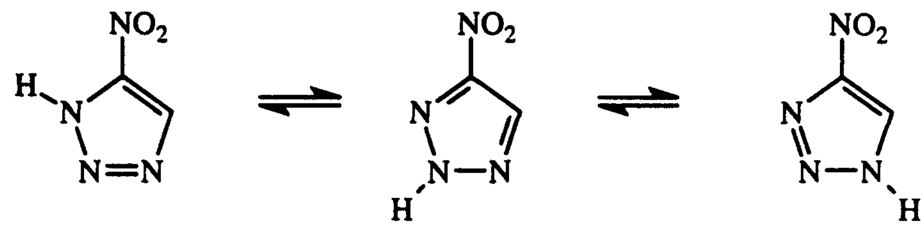


9

We have used density functional methods to compute optimized geometries, dissociation energies and gas phase heats of formation. The N-NF_2 bonds in **4**, **6** and **8** are from 5 to 9 kcal/mole stronger than the corresponding N–NO_2 in **5**, **7** and **9**. The dissociation energies of the other N–NO_2 and the C–NO_2 bonds in these molecules are very little affected (2 - 3 kcal/mole) by replacing N–NO_2 by N–NF_2. Since the cleavage of N–NO_2 bonds is believed to play a key role in the decomposition of many nitramines, it may be that the replacement of >N–NO_2 by >N–NF_2 will improve shock/impact sensitivity. The difluoramine heats of formation are about 16 kcal/mole less positive than those of the corresponding dinitramines.

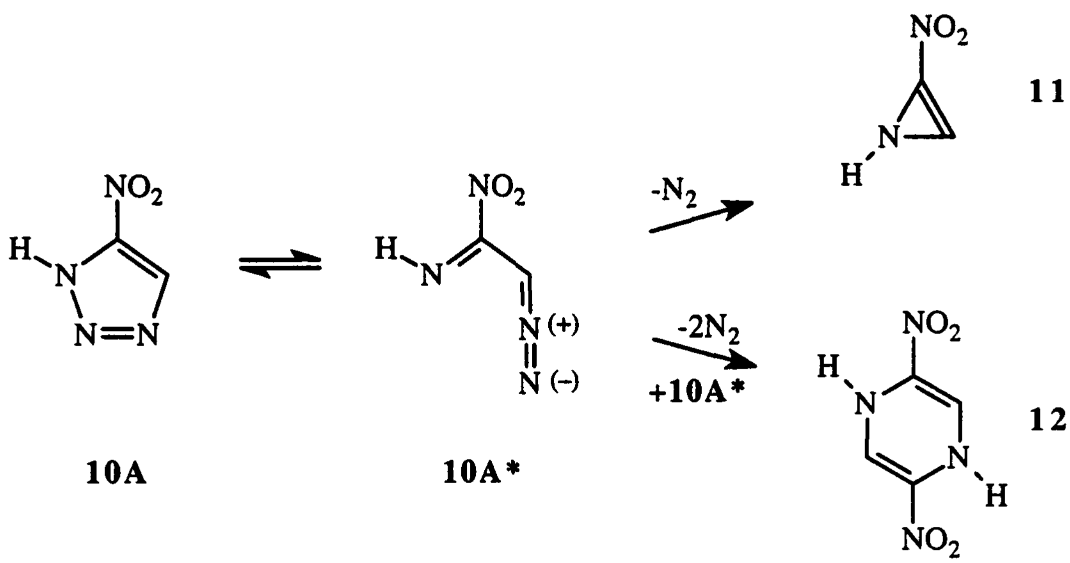
3. Nitro-1,2,3-triazole Sensitivity

In conjunction with our studies of high-nitrogen-content compounds, we have investigated the decomposition of the nitro-1,2,3-triazole **10**, which is known experimentally to be highly sensitive toward impact (h_{50} = 25 cm). This molecule has several tautomeric forms as shown.

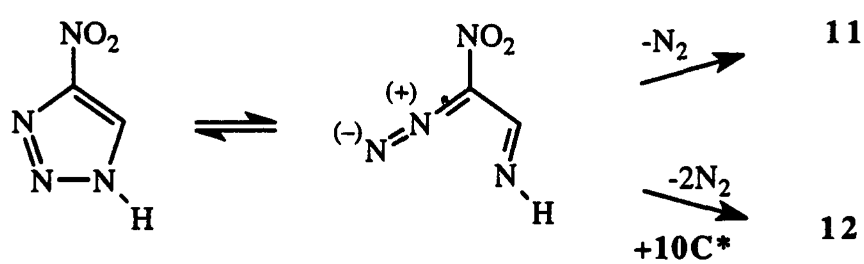


10A 10B 10C

Our density functional analysis shows **10B** to be the most stable, about 3 kcal/mole lower in energy than **10A** and **10C**. Possible decomposition routes for **10A** and **10C**, shown in eqs. (1) and (2), are through the intermediates **10A*** and **10C*** (suggested by J. H. Boyer) and proceeding to either **11** or **12**. (Such a pathway is structurally not available to **10B**.)



10A 10A* (1)



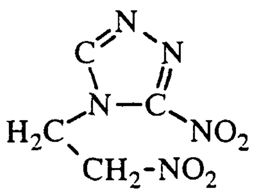
10C 10C* (2)

We found that the energetics of the individual steps are essentially identical in eqs. (1) and (2), and that **12** is thermodynamically greatly favored over **11** as the final product. The initial step, **10A**

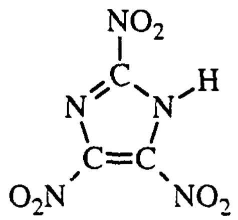
→ 10A* or **10C** → 10C*, requires an energy input of 16 kcal/mole; however the formation of **12** is quite exothermic, to the extent that the overall reaction, **10A** → **12** or **10C** → **12**, releases 34 kcal per mole of **10A** or **10C**. (Relative to **10B**, the energy release would be 31 kcal/mole.) The energy needed to initiate these processes, to form **10A*** or **10C***, is relatively low when it is considered that the decomposition of many energetic materials is believed to begin with the rupture of a C–NO_2 or N–NO_2 bond, which typically requires at least 40 kcal/mole. Furthermore, there is a significant net release of energy when **10A** → **12** or **10C** → **12**, which can promote further decomposition. This appears, therefore, to be a reasonable interpretation of the high sensitivities that have been observed for the nitrotriazole **7** and for analogous compounds.

4. Prediction of Macroscopic Properties

In earlier work, we have shown that a variety of macroscopic properties can be correlated and predicted in terms of certain key computed quantities, most of which are related to the electrostatic potential on the molecular surface. We have now extended this approach to include properties of interest to the energetic materials program, such as liquid and solid densities and heats of vaporization, as well as impact sensitivities of nitroheterocycles. In the latter area, we have developed a relationship which correlates the impact sensitivities over a wide range, from very high for **13** to very low for **18**.



13



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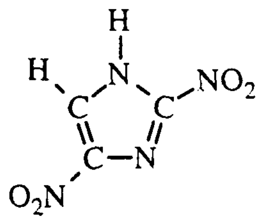

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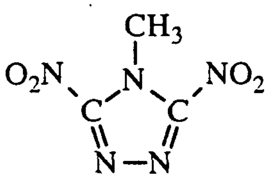

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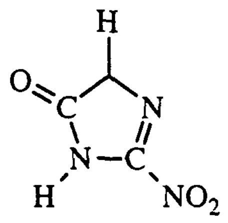

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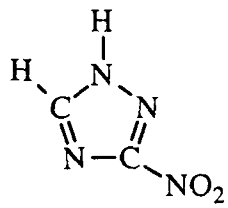

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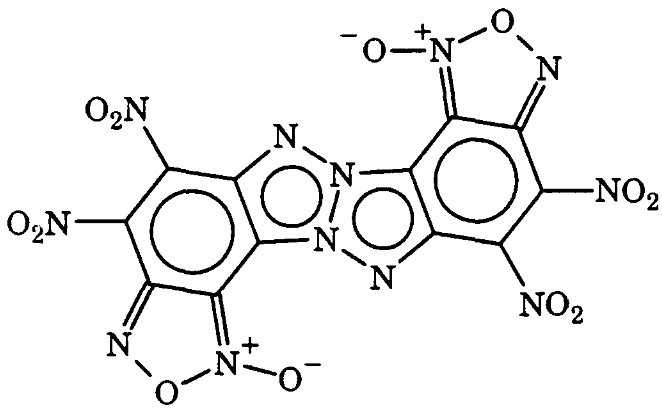
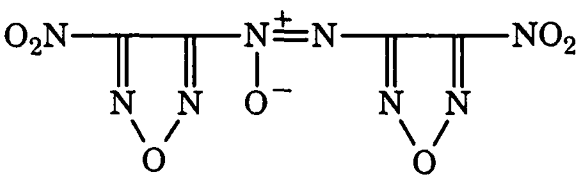
PLANS FOR NEXT YEAR'S RESEARCH

1. <u>Prediction of Heats of Formation and Other Properties for New and Proposed Energetic Compounds:</u>

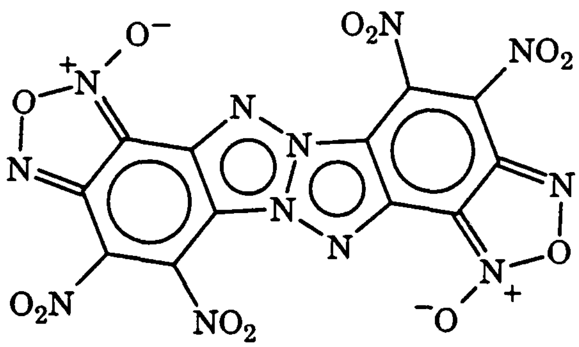
We will continue to compute heats of formation and other important properties (heats of fusion and vaporization, melting and boiling points, etc.) for compounds related to the energetic materials program of ONR. Such calculations are already underway or will soon begin for the following compounds:



19, BTBB, $C_{12}N_{12}O_{12}$



20, DNAF



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Department of Chemistry
New Orleans, LA 70148
(504) 286-6311
(504) 286-6860 FAX

University of New Orleans
SHAPING OUR FUTURE

September 29, 1994

Defense Technical Information Center
Bldg. 5, Cameron Station
Alexandria, VA 22314

Dear Sir or Madam,

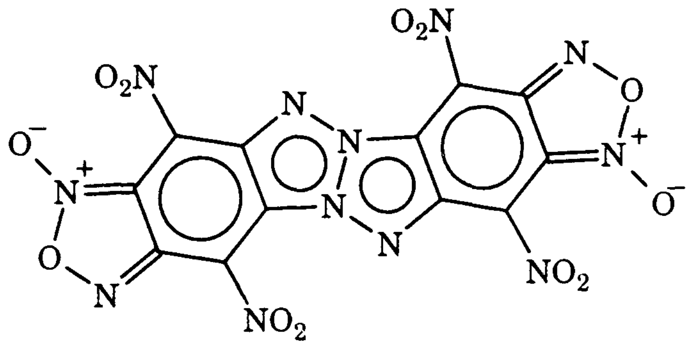
I enclosed two copies of the End-of-Fiscal-Year Report on ONR contract number N00014-91-J-4057.

This support was very greatly appreciated.

Sincerely,

Peter Politzer
Boyd Professor of Chemistry

PP/ahb



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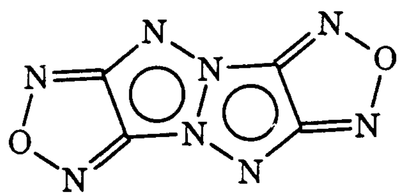
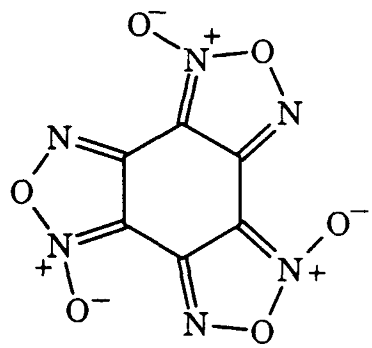


23



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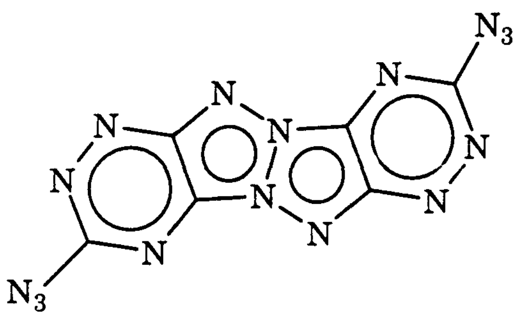
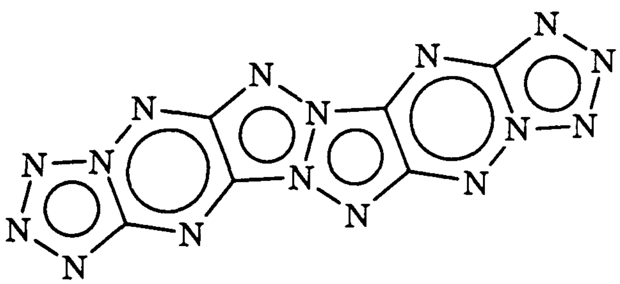
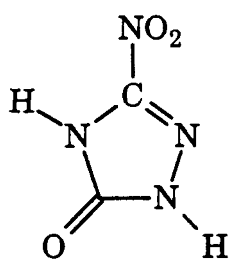


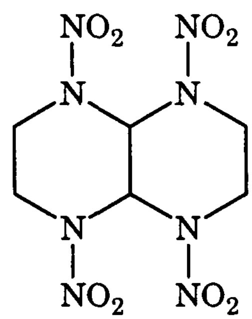
25



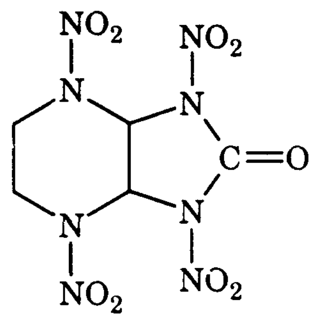
26



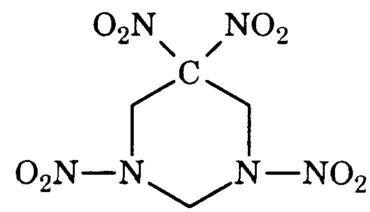
27, NTO



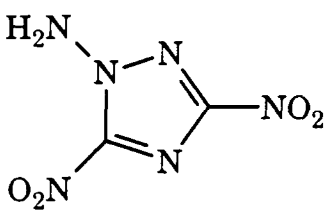
28, TNAD



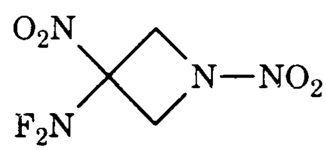
29, K-56



30, TNDA



31, ADNT

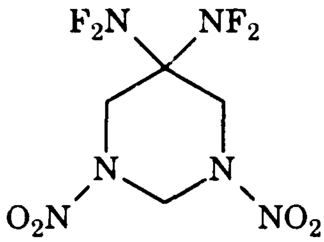


32

Comments: **19** and **20** have already been prepared by J. H. Boyer. **21** and **22** are isomers of **19**, which may be involved in equilibria with it; the primary interest here is in the relative stabilities of **19**, **21** and **22**. **23** and **24** are current target compounds of the Boyer-Trudell synthesis program. **25** and **26** have been proposed by M. L. Trudell. Heats of formation and other calculated properties for **27** - **30** have been requested of us by B. Finck (SNPE, France). **31** has been prepared by Schmitt and Bottaro (SRI). **32** has been included because it has an unusually large value for the number of gaseous molecules produced per unit weight, suggesting excellent potential as a propellant.

2. *gem*-Difluoramines:

We have already begun an investigation of *gem*-difluoramines, by computing the optimized geometry of the RDX analog **33**. This will be extended to include such compounds as **34** - **36**. We will ascertain whether their optimized structures correspond to energy minima (thus assuring their potential existence) and then determine their heats of formation and other properties of interest, such as C–NO_2 and C–NF_2 dissociation energies, sensitivities and activation energies for decomposition. This will complement the work that we have just finished on >N–NF_2 systems.



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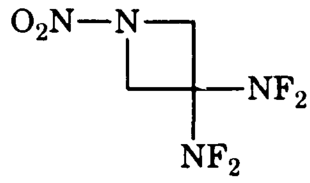

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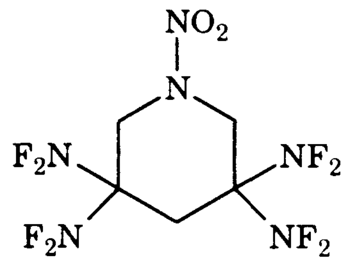

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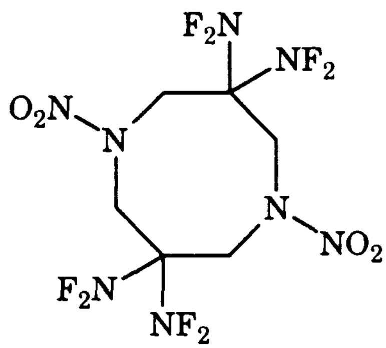

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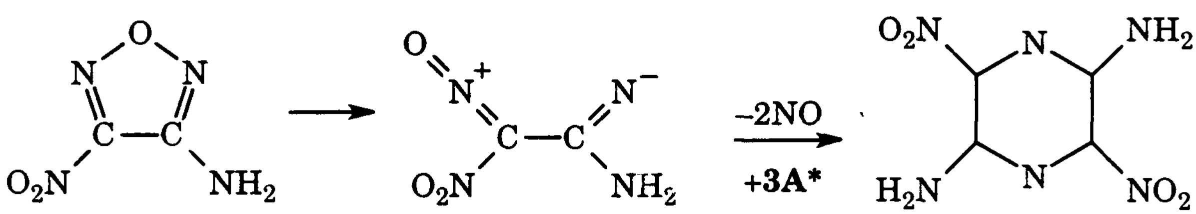
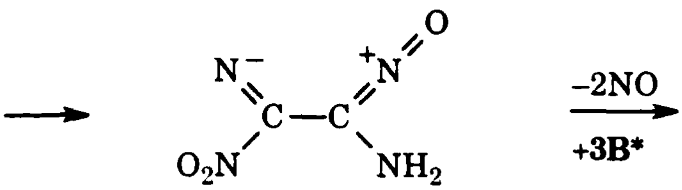
3. <u>Nitrofurazan Sensitivity</u>

As an extension of our work on nitro-1,2,3-triazole, described earlier in this report, we will analyze the decomposition of amino-nitrofurazan, **3**. This compound is also known to be very sensitive toward impact (h_{50} = 27 cm). We will investigate the energetics of the processes described in eqs. (3) and (4); these are analogous to eqs. (1) and (2) for the nitro-1,2,3-triazole. Our objectives are to elucidate the special mechanisms responsible for the very high sensitivities of nitro derivatives of furazans and of 1,2,3-triazoles; these compounds are characterized by linkages involving three highly electronegative atoms (oxygen and nitrogens).



(3)

3 **3A*** **37**

3  37 (4)

3B*

4. General Shock/Impact Sensitivities:

We shall continue to develop relationships for correlating and predicting shock and impact sensitivities from our set of computed molecular quantities. We shall broaden our scope to include other types of energetic compounds, such as nitramines, and we will also try to generalize our relationships so that they are not limited to only specific classes of compounds. Since one of the problems in this area is obtaining reliable and consistent measured sensitivities, we have contacted J. R. Stine (Los Alamos National Laboratory), who has been active in this field for some years, and who has agreed to provide us with additional experimental data.

TECHNOLOGY TRANSFER

Technology	Transferee
♦ Techniques for prediction of shock/impact sensitivities and other macroscopic properties of energetic compounds.	B. Finck, G. Eck (SNPE, France)
♦ Reaction energetics for decomposition of 1,3,3-trinitroazetidine, nitramide, $HN(NO_2)_2$, $N(NO_2)_2^-$ and 1,3-dinitro-1,3-diazacyclobutane.	R. V. Browning (Los Alamos)
♦ Heats of formation of energetic compounds.	J.-F. Danel (CEA, France)
♦ Structures, stabilities and other energetic properties of $N(NO_2)_2^-$ and $HN(NO_2)_2$.	R. J. Schmitt (SRI)
♦ Energetics of thermal decomposition routes of $N(NO_2)_2^-$	R. J. Doyle T. P. Russell (NRL)
♦ Heat of formation and specific impulse of a nitro-oxadiazolyl-triazolo-oxadiazole (NOTO).	J. H. Boyer (UNO)
♦ Energetics of decomposition routes of 1,3,3-trinitroazetidine	Y. T. Lee (UC-Berkeley)
♦ Structures and stabilities of several proposed high-nitrogen energetic compounds, some of which were subsequently prepared.	J. H. Boyer (UNO)
♦ Structures and relative stabilities of isomers proposed as RDX decomposition products.	R. Behrens (Sandia)
♦ Structure and reactive behavior toward nucleophile of precursor in ammonium dinitramide synthesis.	A. Stein (ONR)
♦ Structures and surface electrostatic properties of three C, N, H-molecules having highest crystal densities known for unsubstituted compounds.	R. Gilardi (NRL)

LIST OF PUBLICATIONS/REPORTS/PRESENTATIONS

1. Papers Published in Refereed Journals:

(1) "Chemical Applications of Molecular Electrostatic Potentials"
P. Politzer and J. S. Murray, Trans. Amer. Cryst. Assoc., Vol. 26, 23 (1990).

(2) "Anomalous Stabilizing and Destabilizing Effects in Some Cyclic π-electron Systems"
P. Politzer, M. E. Grice, J. S. Murray, and J. M. Seminario, Can. J. Chem., 71, 1123 (1993).

(3) "Density Functional Study of the Structure and Some Decomposition Reactions of the Dinitramide Anion, $N(NO_2)_2^-$"
P. Politzer, J. M. Seminario, M. C. Concha and P. C. Redfern, J. Mol. Struct. (Theochem), 287, 235 (1993).

(4) "Computational Study of the Structure of Dinitraminic Acid, $HN(NO_2)_2$, and the Energetics of Some Possible Decomposition Steps."
P. Politzer and J. M. Seminario, Chem. Phys. Lett., 216, 348 (1993).

(5) "Does Antiaromaticity Imply Destabilization?"
J. S. Murray, J. M. Seminario and P. Politzer, Int. J. Quantum Chem., 49, 575 (1994).

(6) "Calculated Structure, Heat of Formation and Decomposition Energetics of 1,3-Dinitro-1,3-Diazacyclobutane"
M. E. Grice, D. Habibollahzadeh and P. Politzer, J. Chem. Phys., 100, 4706 (1994).

(7) "Antiaromaticity in Relation to 1,3,5,7-Cyclooctatetraene Structures"
P. Politzer, J. S. Murray, J. M. Seminario, Struct. Chem., 50, 273 (1994).

(8) "Molecular Surface Electrostatic Potentials in the Analysis of Non-Hydrogen-Bonding Noncovalent Interactions"
J. S. Murray, K. Paulsen and P. Politzer, Proc. Ind. Academy of Sciences, 106, 267 (1994).

2. Papers Accepted for Publication and in Press:

(1) "Non-local Density Functional Calculation of Gas Phase Heats of Formation"
D. Habibollahzadeh, M.E. Grice, M. C. Concha, J. S. Murray and P. Politzer, J. Comp. Chem., in press.

3. Papers Submitted for Publication:

(1) "A Density Functional Analysis of a Decomposition of 4-Nitro-1,2,3-Triazole Through the Evolution of N_2"
P. Politzer, M.E . Grice and J. M. Seminario, J. Phys. Chem., submitted.

(2) "Computed Structures and Bond Dissociation Energies of Difluoramino Derivatives"
P. Politzer, P. Lane, J. S. Murray, M. E. Grice, M. C. Concha and P. C. Redfern, J. Mol. Struct. (Theochem), submitted.

4. Book Chapters Published:

   none

5. Book Chapters in Press:

   (1) "Computational Studies of Energetic Organic Molecules"
   P. Politzer and J. S. Murray, in Organic Energetic Compounds, P. Marinkas, ed., Nova Science Publishers, New York, in press.

   (2) "Density Functional Studies of Decomposition Processes of Energetic Molecules"
   P. Politzer, J. M. Seminario and M. E. Grice, in *Modern Density Functional Theory*, J. M. Seminario and P. Politzer, eds., vol. 2, Elsevier, Amsterdam, in press.

6. Technical Reports and Non-refereed Papers:

   (1) "Computational Studies of Energetic Organic Molecules"
   P. Politzer and J. S. Murray, in Organic Energetic Compounds, P. Marinkas, ed., Nova Science Publishers, New York, in press.

   (2) "Molecular Surface Electrostatic Potentials in the Analysis of Non-Hydrogen-Bonding Noncovalent Interactions"
   J. S. Murray, K. Paulsen and P. Politzer, Proc. Ind. Academy of Sciences, 106, 267 (1994).

   (3) "Does Antiaromaticity Imply Destabilization?"
   J. S. Murray, J. M. Seminario and P. Politzer, Int. J. Quantum Chem., 49, 575 (1994).

   (4) "Computational Study of the Structure of Dinitraminic Acid, $HN(NO_2)_2$, and the Energetics of Some Possible Decomposition Steps."
   P. Politzer and J. M. Seminario, Chem. Phys. Lett., 216, 348 (1993).

   (5) "Antiaromaticity in Relation to 1,3,5,7-Cyclooctatetraene Structures"
   P. Politzer, J. S. Murray, J. M. Seminario, Struct. Chem., 50, 273 (1994).

   (6) "Calculated Structure, Heat of Formation and Decomposition Energetics of 1,3-Dinitro-1,3-Diazacyclobutane"
   M. E. Grice, D. Habibollahzadeh and P. Politzer, J. Chem. Phys., 100, 4706 (1994).

7. Presentations:

   (1) "Computational Contributions to the Development of New Energetic Materials," ONR Meeting, Los Alamos, NM, November 1993.

   (2) "Computational Studies of Molecular Interactions: General Interaction Properties Function (GIPF)," Texas Technological University, Lubbock, TX, March 1994.

   (3) "Computational Approaches to the Prediction of Shock/Impact Sensititivies"
   Gordon Conference on Energetic Materials, New Hampton, NH, June 1994.

LIST OF HONORS

Peter Politzer:

(1) Promoted to Boyd Professor of Chemistry, the Highest Professorial Rank in the Louisiana State University system, in October 1993.

(2) President, Environment and Health Council of Louisiana.

OTHER CURRENT SPONSORED RESEARCH

(1) "Analysis of Factors Affecting Chemical Reactions in Supercritical Fluids" Office of Naval Research, May 1991 - November 1994. $604,728.

(2) "Characterization of Compounds through Computed Molecular Surface Quantitites" Sterling-Winthrop, January 1994 - indefinite. $47,000.

(3) "Development of Computer Code to Predict Sensitivity of Chemical Explosives" US Army Research, Deveopment, and Engineering Center through the Battelle Scientific Services Program. March 1994 - October 1994. $18,102.

ESTIMATED FUNDING BALANCE

The ONR grant/contract resources that remain at our institution as of 30 September 1994 are $709.56. This amount is left in indirect costs and is due to a change in the indirect cost rate from 44% to 41%. There is nothing left in direct costs.

DEGREES GRANTED:

None.